

2005 DOE Hydrogen Program Review  
**Sulfur-Iodine Thermochemical Cycle**

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# Overview

## Timeline

- Start - 9/2002
- Finish - 9/2008
- ~ 25% complete

## Budget

- Funding
  - DOE – 4.2 M\$
  - CEA In kind
- FY04 Funding – 1.4 M\$
- FY05 Funding – 2.8 M\$

## Barriers

- Materials – high temperature, corrosive environments
- Process chemistry, thermodynamic data
- Reactor to process interface

## Partners

- Process – CEA, SNL, General Atomics
- Supporting Technology – INL, ORNL, ANL, UNLV, MIT, UCB, Ceramatec

# Sulfur Iodine Thermochemical Cycle

## Objectives

- Investigate the potential of the Sulfur-Iodine cycle for Hydrogen production using nuclear energy
  - Flowsheet analysis of process options
  - Design and construct lab scale experiments for the three major reaction sections of the S-I cycle
    - *Lab scale experiments on  $H_2SO_4$  and HIx decomposition, and primary (Bunsen) reaction*
    - *Investigate process alternatives, materials, catalysts, diagnostics, membrane applications*
  - Utilize engineering materials where feasible
  - Integrate component sections and perform a closed loop experiment in final phase
  - Provide basis for pilot scale experiment design

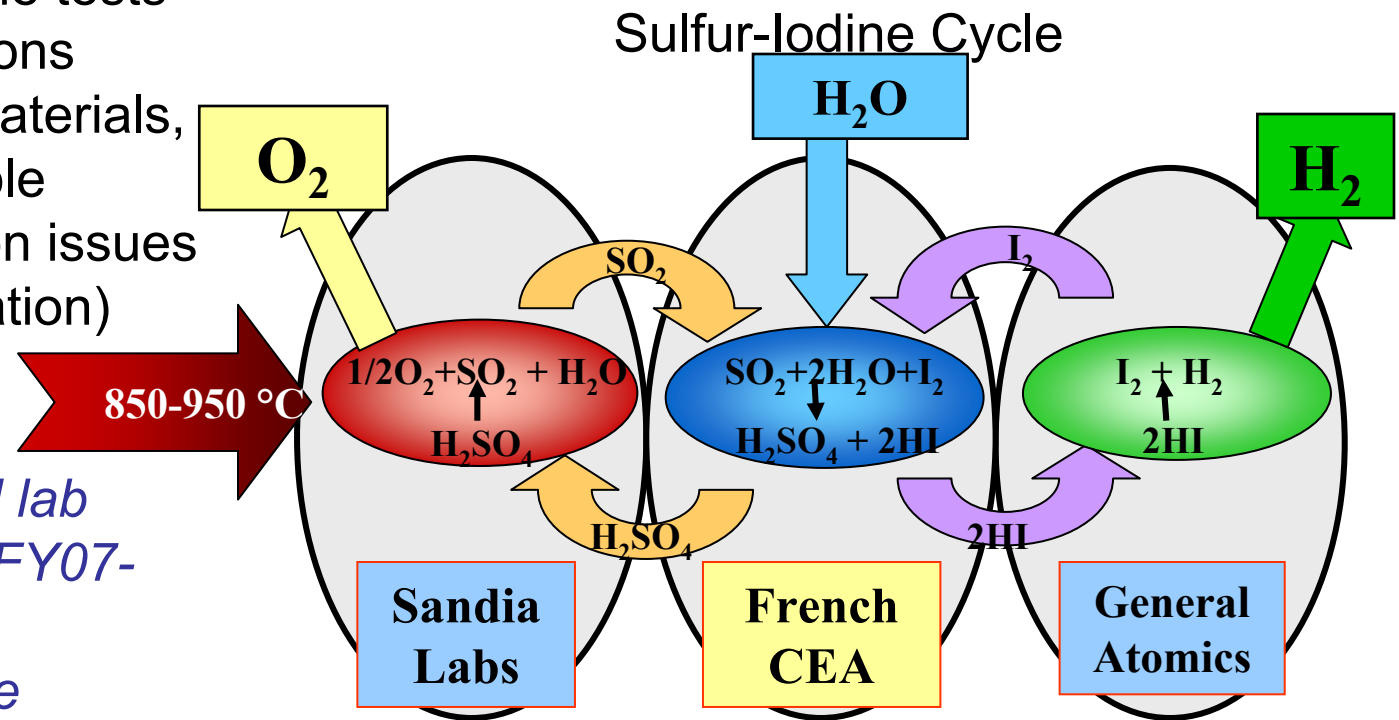
# Sulfur Iodine Thermochemical Cycle

## Lab Scale Experiment – Approach

- Perform flowsheet analyses of process alternatives
- Construct reaction sections using initial materials

- Perform stand alone tests on component sections
- Utilize improved materials, catalysts, as available
- Evaluate integration issues (controls, contamination)

- *Perform integrated lab scale experiments (FY07-FY08)*
- *Basis for pilot scale experiment design*



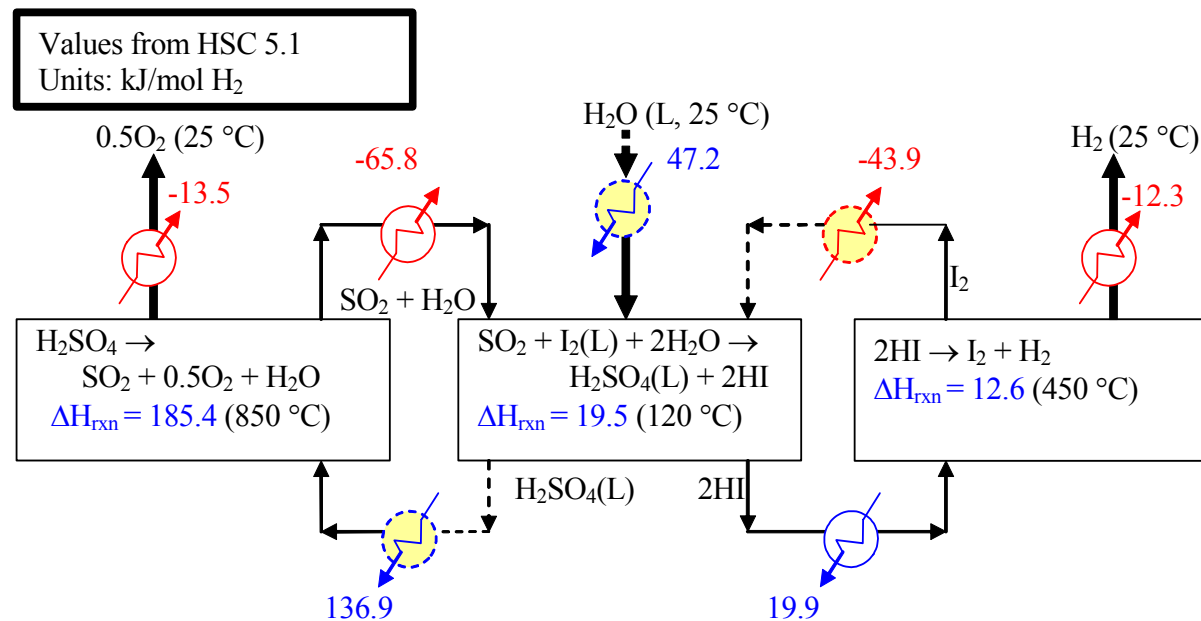
- *HI section (GA)*
- *H<sub>2</sub>SO<sub>4</sub> Section (SNL)*
- *Bunsen (CEA)*
- *Materials (INL, ORNL, Univ, Industry)*

# Technical Accomplishments/ Progress/Results Summary

- Completed flowsheet analysis of alternate S-I configurations
- Designed and constructed test apparatus for component reactions ( $\text{H}_2\text{SO}_4$ , Hx, Bunsen)
- Experiments initiated for component reaction sections
  - $\text{H}_2\text{SO}_4$  decomposition section (boiler, decomposer) engineering materials (started 12/2004, 850 C at ambient pressures)
  - Reactive distillation Hx decomposition section
    - Reactive distillation (started 2/2005, >20-35 bar, 250 C, glassware in pressure vessel)
    - Extractive distillation (started 4/2005)
  - Bunsen reactor section (started 2004, glassware exps, engineering materials apparatus, scheduled 9/2005, CEA)
- Thermophysical property measurements – HI/I<sub>2</sub>/H<sub>2</sub>O vapor-liquid equilibrium measurements initiated (CEA)
- Preliminary integrated lab scale experiment designs

# Flowsheet Analysis for Thermochemical Processes

- Simulate process configuration and conditions (ASPEN)
  - First step in process design, evaluation
  - Characterize process energy and stream flows (T, P, F<sub>i</sub>)
  - Calculation of energy/heat requirements, efficiency

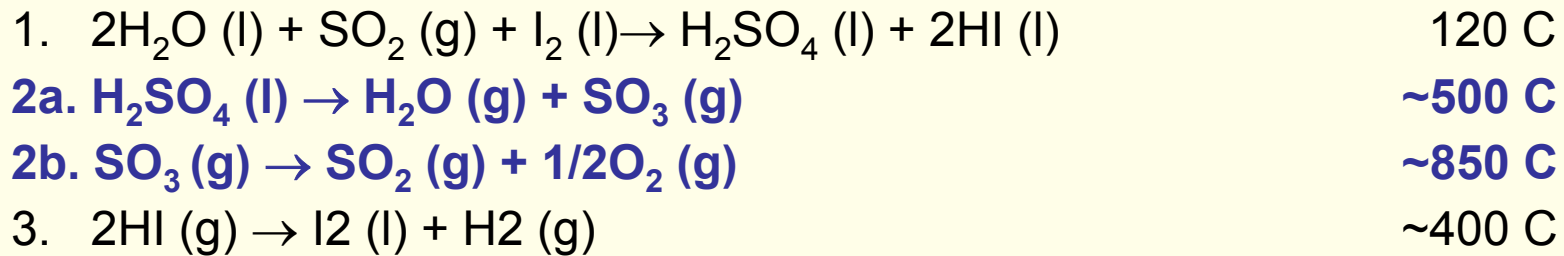


- Evaluation of process alternatives, uncertainties
  - System optimization, parameter studies
  - Some alternatives incorporated, others being evaluated experimentally
  - First step in defining component sizes and quantities -- costs

# Flowsheet Options for Laboratory Scale Sulfur-Iodine Sections

Process Section	Alternative 1	Alternative 2	Selection
<b>Section 1 (Bunsen)</b>	<b>Co-current Bunsen</b> <ul style="list-style-type: none"> <li>- Short residence time</li> <li>- Efficient HX</li> <li>- No side reactions</li> <li>- Previously demonstrated</li> </ul>	<b>Counter-current Bunsen</b> <ul style="list-style-type: none"> <li>- Fewer pieces of equipment</li> <li>- Fewer streams</li> <li>- Less recycle</li> <li>- Not yet demonstrated</li> </ul>	<b>Counter-current Bunsen</b> <ul style="list-style-type: none"> <li>- Less recycle, less complex, selected by CEA</li> </ul>
<b>Section II (H<sub>2</sub>SO<sub>4</sub>)</b>	<b>HP Flash/Vacuum Still</b> <ul style="list-style-type: none"> <li>- higher concentration ~90 mole % H<sub>2</sub>SO<sub>4</sub></li> <li>- less efficient</li> </ul>	<b>Direct contact HX</b> <ul style="list-style-type: none"> <li>- Direct contact heat /mass exchange</li> <li>- Heat required reduced ~5 to 10%</li> <li>- Eliminates vacuum still</li> </ul>	<b>Direct Contact HX</b> <ul style="list-style-type: none"> <li>- Reduced heat demand</li> <li>- SO<sub>3</sub> recovery</li> </ul>
<b>Section III (H<sub>2</sub>O)</b>	<b>Extractive distillation</b> <ul style="list-style-type: none"> <li>- Use H<sub>3</sub>PO<sub>4</sub> or HBr to extract water</li> <li>- Vapor recompression (heat pumps) required for H<sub>3</sub>PO<sub>4</sub></li> <li>- HBr too costly under optimistic assumptions</li> <li>- Basic H<sub>3</sub>PO<sub>4</sub> steps demonstrated</li> </ul>	<b>Reactive Distillation</b> <ul style="list-style-type: none"> <li>- Less equipment, fewer streams</li> <li>- More recycle</li> <li>- heat pumps required</li> <li>- Not demonstrated</li> <li>- Similar heat and energy requirements</li> </ul>	<b>Reactive Distillation</b> <ul style="list-style-type: none"> <li>- Experiment baseline</li> </ul> <b>H<sub>3</sub>PO<sub>4</sub> Extractive distillation</b> <ul style="list-style-type: none"> <li>- Backup process</li> </ul>

# Sulfuric Acid Section



- Concentrate dilute acid from Bunsen reaction (1), decompose to  $\text{SO}_3$ , and  $\text{SO}_2$  and  $\text{O}_2$ .  $\text{SO}_2$  and  $\text{H}_2\text{O}$  input to Bunsen. Accounts for most of the thermal input requirement
- Key Issues
  - High temperature process heat exchanger(s)
  - Materials – corrosion, temperature, catalyst activity
  - Energy efficiency - recuperation
- Options
  - Vacuum distillation
  - Direct contact HX – more heat efficient, eliminates vacuum still
- Sequence / approach
  - Construct initial section from best estimate materials, catalysts
  - Develop diagnostics, refine design, materials,
  - longer term materials and ceramic component development



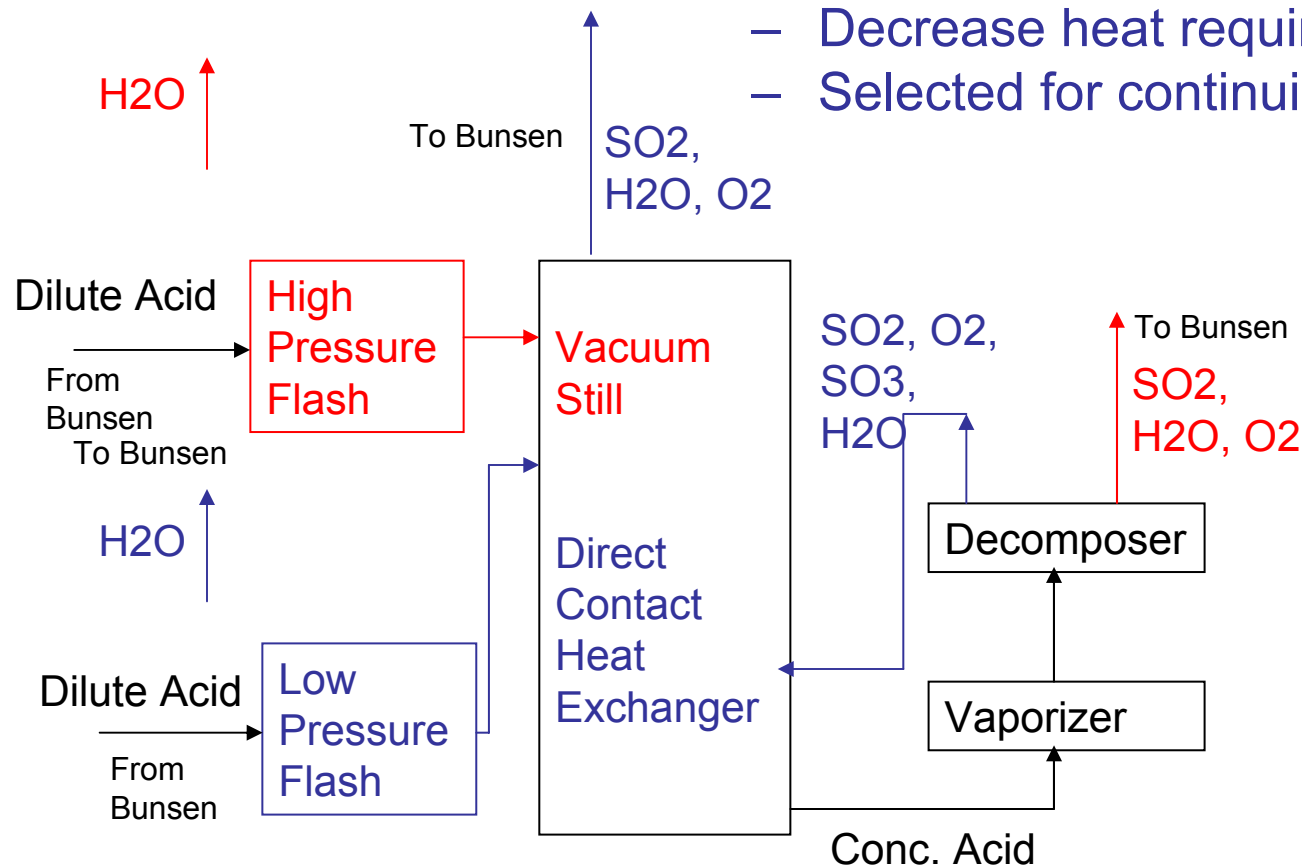
# H2SO4 Decomposition Section Alternatives

- Vacuum Distillation

- Recover heat from high pressure flash to vacuum distillation

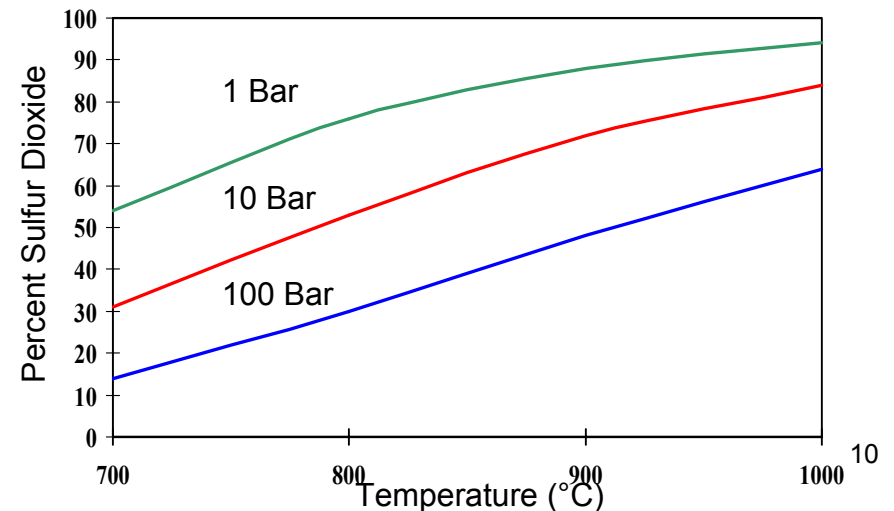
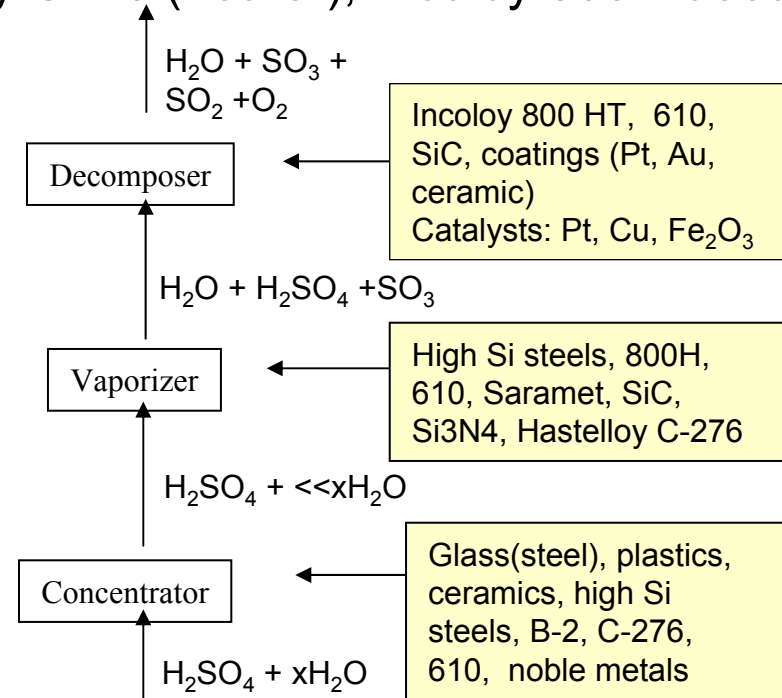
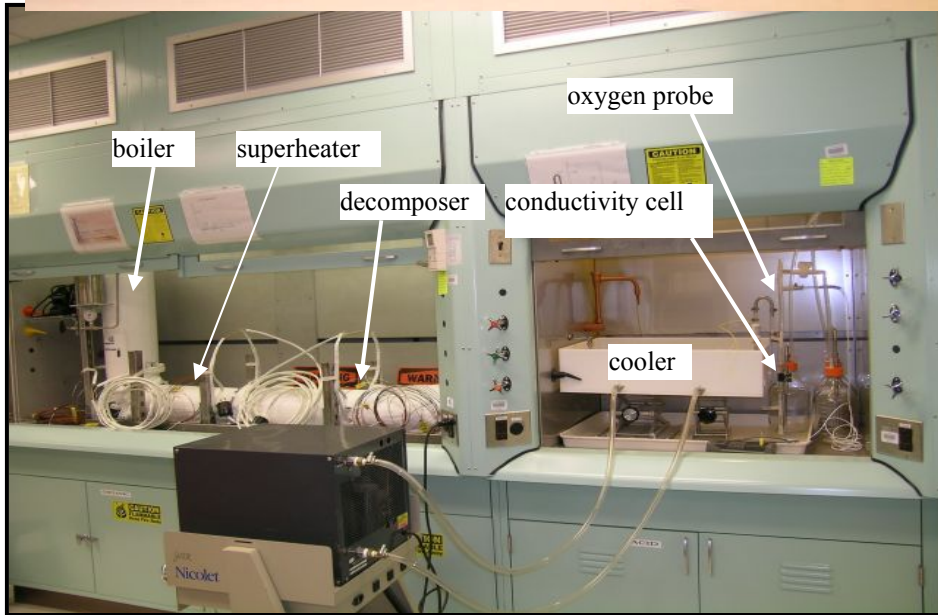
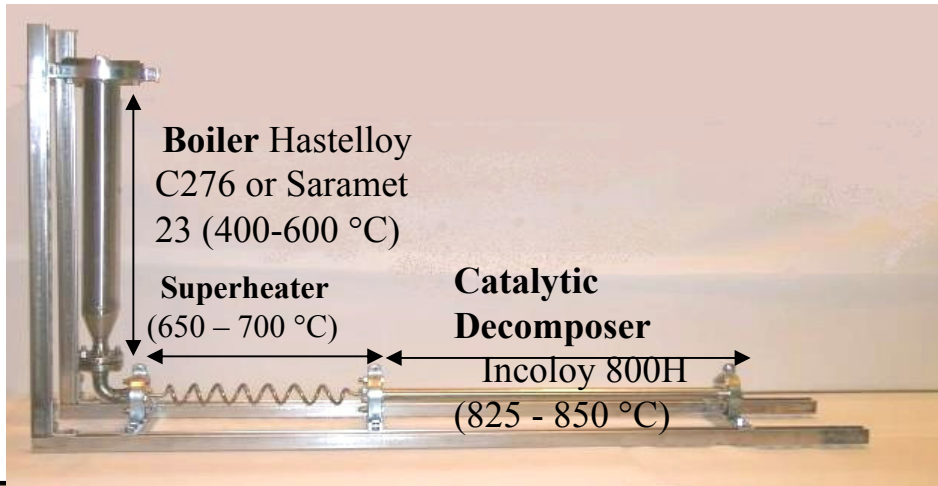
- Direct Contact Heat Exchange

- Vacuum flash using low temperature waste heat
- Additional concentration in high pressure DCHX recuperator
- Decrease heat requirement
- Selected for continuing work



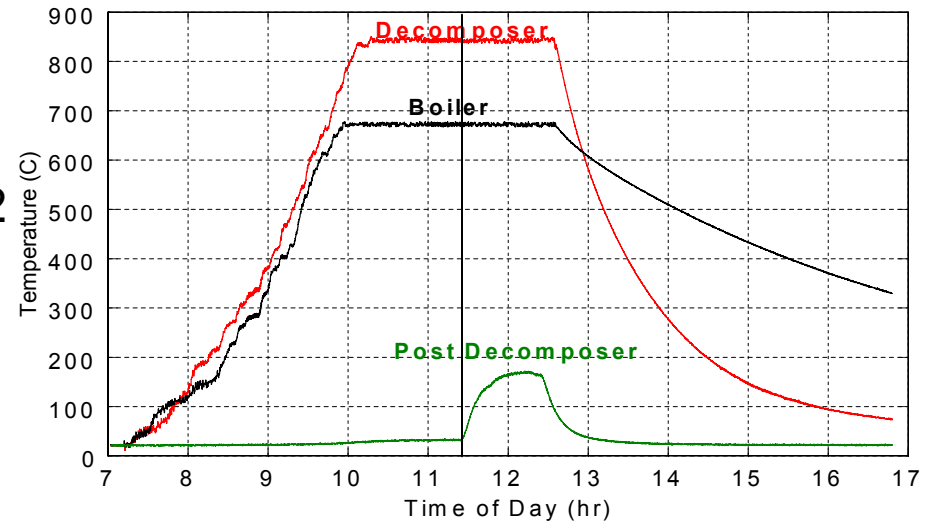
# Sulfuric Acid Section -- Status

- Completed construction of modular acid decomposition apparatus (Saramet boiler, Hastelloy C276 (heater), Incoloy 800H decomp.



# Sulfuric Acid Section -- Status

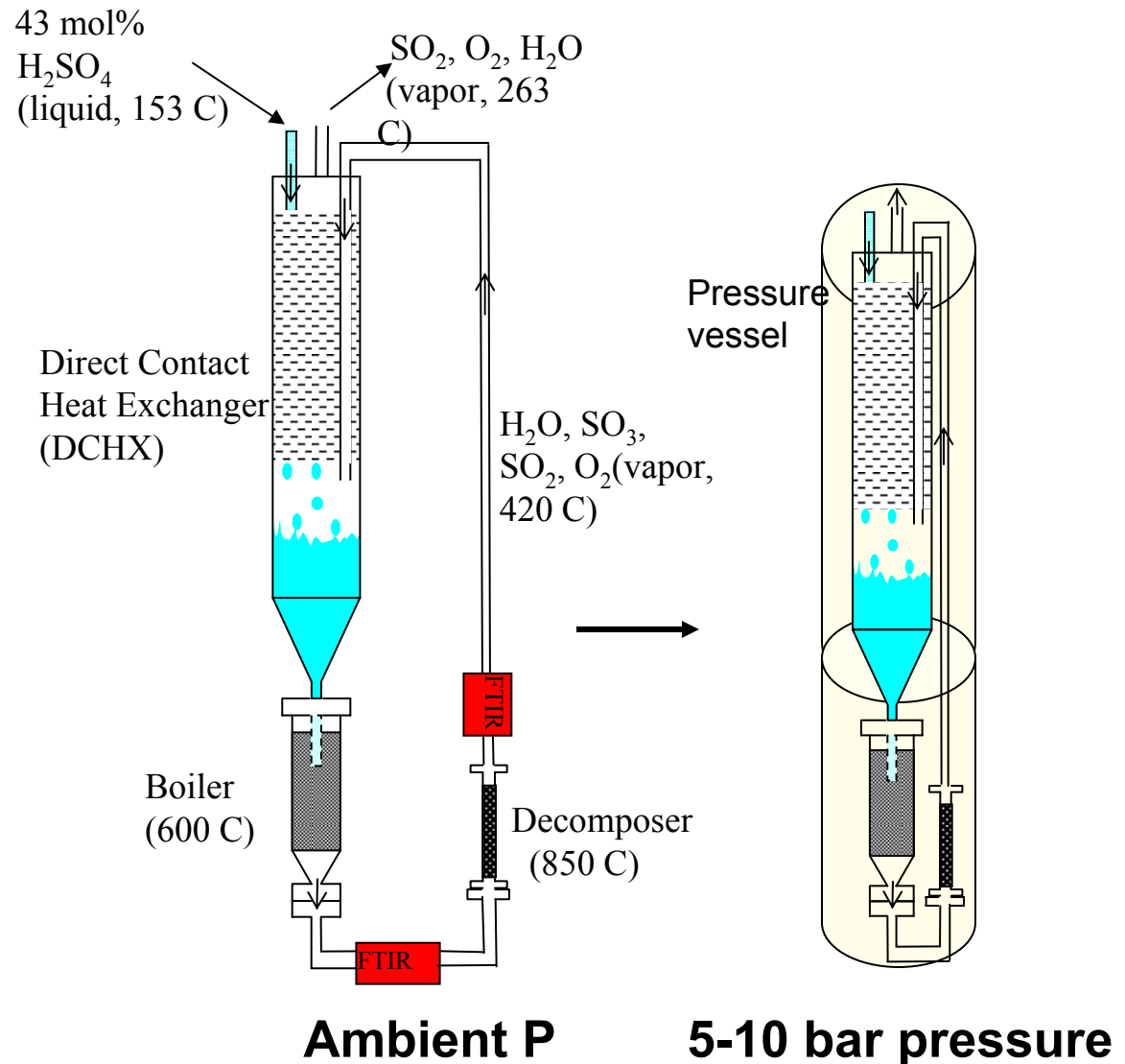
- Completed two acid tests at 850 C (ambient pressure)
  - Limited corrosion in vapor phase and cold liquid sections
  - Significant corrosion in boiling, condensing sections, qualitatively more severe than estimated static vs flow, SO<sub>2</sub>
  - Boiler (ceramic bed) temperature increased to limit corrosion, straight-through configuration



Species	Corrosion Products	Incoloy 800H	Saramet 23	Hast. C276
Cr	10 g/L	21%	18%	16%
Ni	8.0 g/L	32%	17%	57%
Fe	6.6 g/L	40%	55%	5%
Si	0.042 g/L	<5%	5%	<0.08%
Mo	0.26 g/L		0.06%	16%
Au	0.0000046	0	0	0

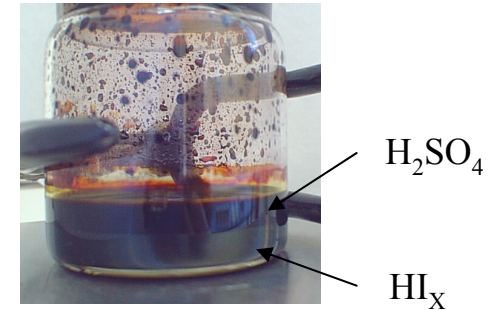
# Sulfuric Acid Section – Testing Sequence

- 1.- Direct contact heat exchange (DCHX), glass DCHX, FTIR development
- 2.- DCHX – ambient pressure with concentrator
3. – DCHX, improved components (ceramics)
4. – Pressurized DCHX apparatus



# Section 3 – HI Decomposition

- Lower phase of Bunsen reaction is a mixture of HI - I<sub>2</sub> - H<sub>2</sub>O. This Section separates HI and decomposes it into H<sub>2</sub> and I<sub>2</sub>
- Key Issues
  - Reactive distillation process chemistry
  - Uncertainty in HI/I<sub>2</sub>/H<sub>2</sub>O vapor equilibrium data
  - High recycle water volumes
  - Materials – corrosion, catalysts
- Options
  - Reactive (baseline), Extractive (backup)
- Sequence / approach
  - Evaluate both approaches experimentally, construct initial sections in glassware in pressure vessel (~20-40 bar)
  - Selection May 2005
  - Construct selected section based on best available materials, modify as improved materials tested



## Extractive Distillation

- Process steps demonstrated, not as integrated process
- Extractant rate and concentration limits not established

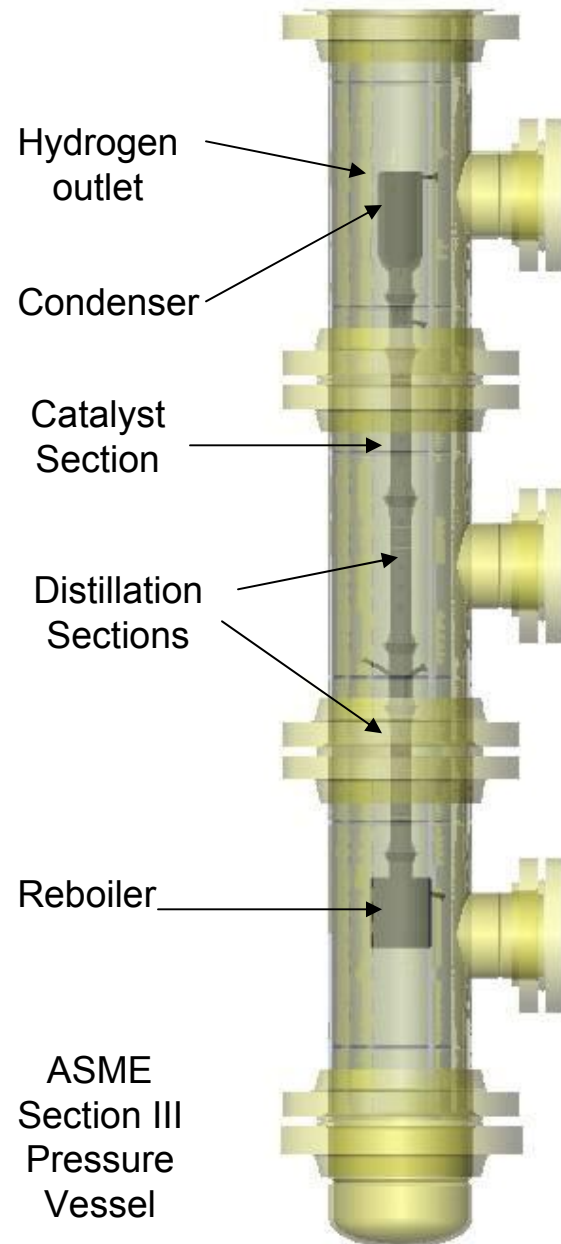
## Reactive Distillation

- Not demonstrated, reactivity of HI under req'd conditions unknown
- Catalyst performance must be determined – rate, deactivation
- Thermophysical data needed



# Initial Reactive Distillation Experiments are in Glass/Metal System

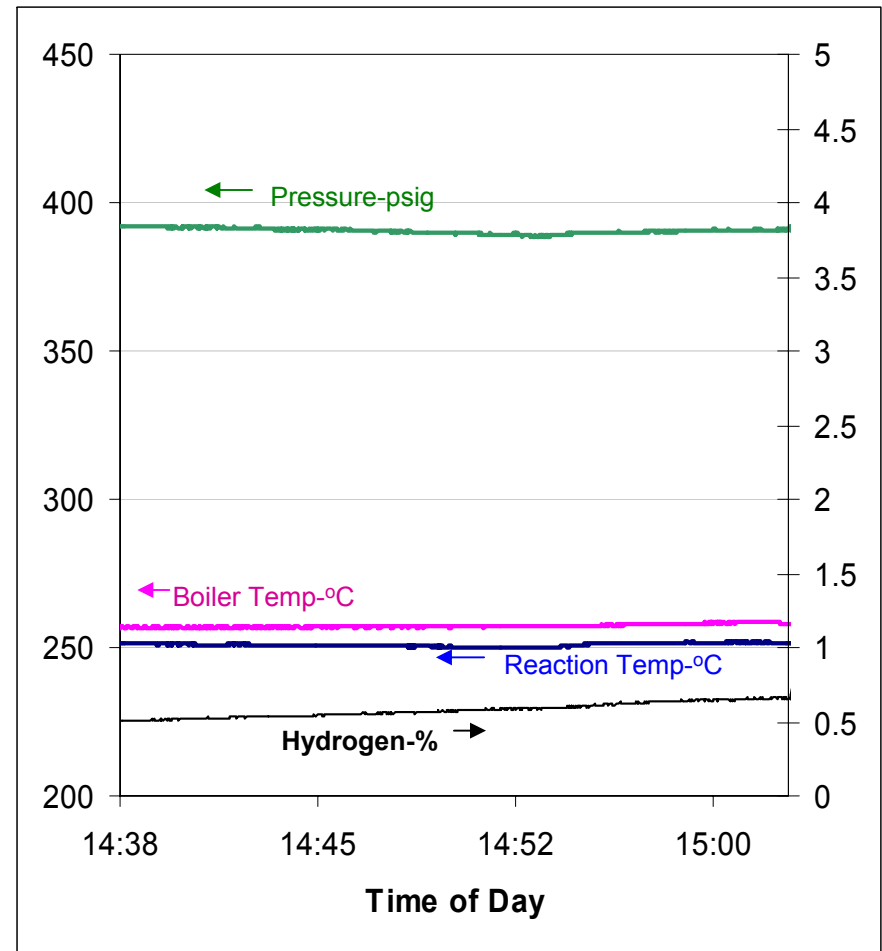
- Process operates at 300-600 psi, 250-300°C
- Distillation separates HI/H<sub>2</sub>O from I<sub>2</sub>
- HI decomposes on catalyst
- Reflux from condenser (HI/H<sub>2</sub>O) washes I<sub>2</sub> from catalyst
- Metallic pressure vessel rated at 625 psig
- Commercial glass distillation column is inexpensive
- Activated carbon catalyst under test
- Hydrogen measured continuously



# Reactive Distillation Results to Date

- Pressure balance system for glass equipment in pressure vessel works well
- Initial HI decomposition experiments begun
  - Focus on reaction kinetics
  - Additional run time required for catalyst life evaluation
- Hydrogen production has been demonstrated
- Lower than expected H<sub>2</sub> production is likely due to slow kinetics and poor catalyst performance

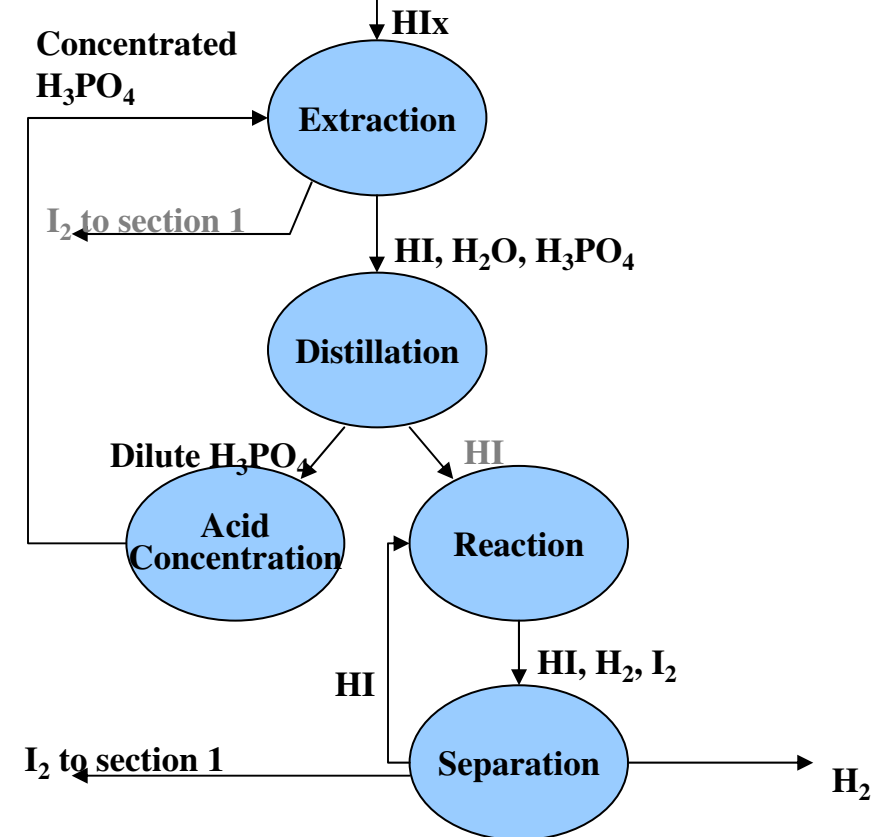
Operating conditions and H<sub>2</sub> production



# Extractive Distillation Experiments

## Initial Experiments Done in Glass System

- Process operates at ambient pressure and 120-450°C
- HI/H<sub>2</sub>O absorbs into the phosphoric acid
- A separate, heavy I<sub>2</sub> phase is formed and returned to the Bunsen reaction
- H<sub>3</sub>PO<sub>4</sub> breaks the HI/H<sub>2</sub>O azeotrope to allow separation of HI from H<sub>2</sub>O and H<sub>3</sub>PO<sub>4</sub>
- Pure HI is decomposed to H<sub>2</sub> and I<sub>2</sub> in a carbon catalyst bed



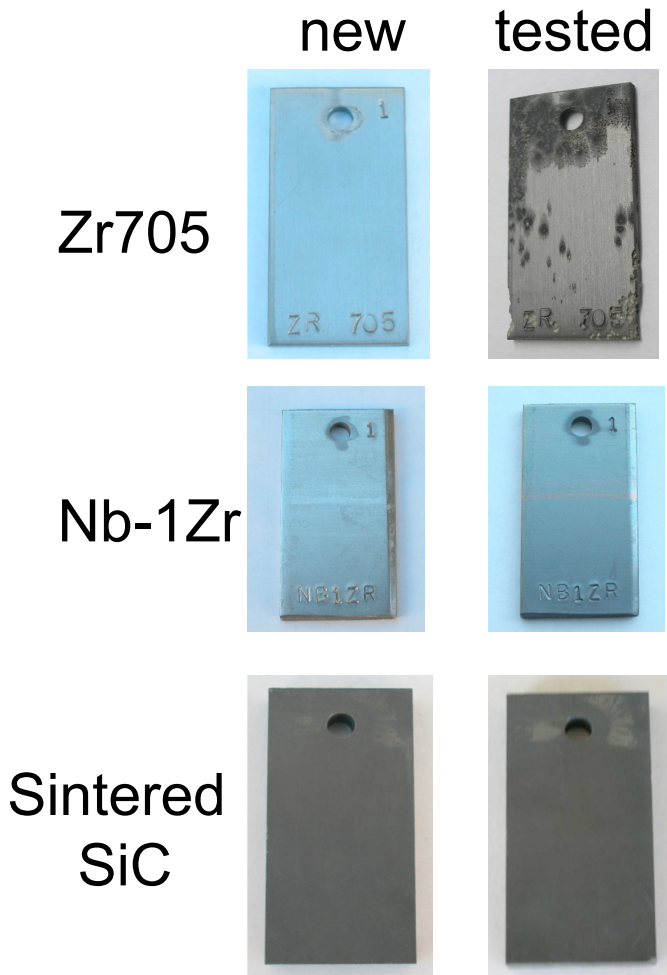
- Status
- Flowsheet simulations completed and used for design of components
- Apparatus assembled and testing started
- April start, support May 15 decision on method for Lab scale exps.





# Materials Testing for Hlx Section

Refractory metals and ceramics have shown the best corrosion performance to date



## Hlx materials testing (UNLV and GA)

- 22 coupons from four classes of materials: refractory and reactive metals, superalloys and ceramics, have been screened.

Excellent	Good	Fair	Poor
Ta-40Nb, Nb-1Zr, Nb-10Hf, SiC(CVD), SiC(Ceram atec sintered), Mullite	Ta, Ta- 10W, Nb, Nb-7.5Ta, SiC (sintered) Si-SiC (3 kinds)	Mo-47Re, Alumina	Mo, C-276, Haynes 188, graphite*, Zr702, Zr705

\* structurally sound but absorbed Hlx

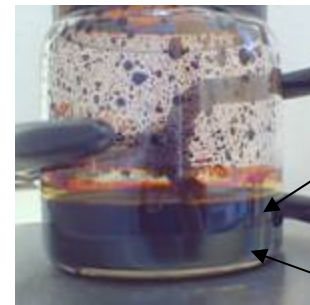
- Long term corrosion performance testing has started
  - effect of  $HI_x$  on stress corrosion
  - cost reduction through cladding

# Bunsen Reaction Section (CEA)

- Bunsen reaction (formation of the two acids in aqueous phases) in optimal conditions for S-I process
- Key Issues
  - Thermal management in reaction column (S formation)
  - Recycle volumes from HI section
  - Thermophysical data uncertain (HI/I<sub>2</sub>/H<sub>2</sub>O -VLE)
  - Materials – corrosion
- Options
  - Co-current (demonstrated), Counter-current (simpler hardware, thermal mgt TBD)
- Sequence / approach
  - Construct glass reactor to determine elemental concentrations in liquid phases
  - Preliminary design of Bunsen section completed
  - First corrosion tests done.

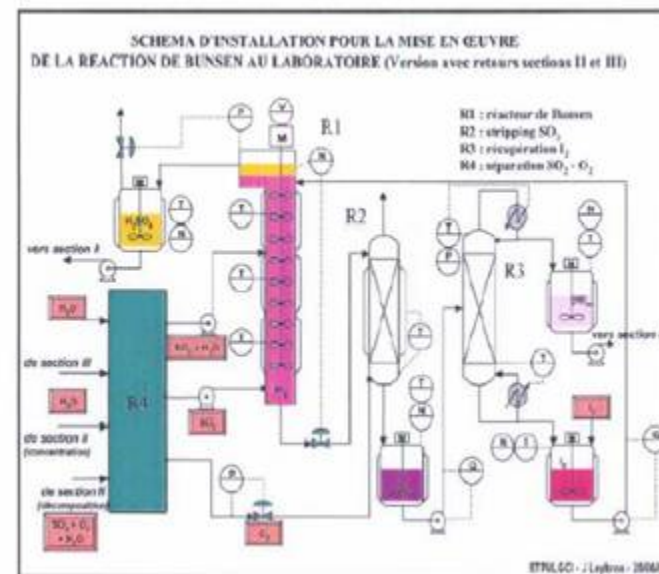
# Bunsen Reaction Section - Status

- Initial Bunsen section exps
- Elemental measurements for determination of total amount of H<sup>+</sup> ions, sulphur and iodine in each phase
- Corrosion tests performed to select appropriate materials
- Preliminary design of Bunsen section
- Complete flowsheet analysis of Bunsen, Hlx section options
- Complete construction of counter-current reactor – 9/05



H<sub>2</sub>SO<sub>4</sub>

HI<sub>x</sub>



Schematic Diagram for Bunsen Reaction



# Supporting Technology Activities

- Materials – high temperature corrosion and mechanical properties – metals, ceramics (UNLV, GA, MIT, ORNL)
- High temperature systems interface – innovative heat exchanger designs, analysis (UNLV, UCB, Ceramatech)
- Membranes – high temperature inorganic membranes for acid decomposition (ORNL)
- SO<sub>3</sub> decomposition - electrolysis (ANL)
- Membranes for water separation (INL)
- Acid decomposition - catalysts (INL)

# Sulfur Iodine Thermochemical Cycle

## Planned Activities (FY05-FY08)

- FY05 – Complete component reaction section preparations and initial testing
  - Complete acid decomposer ambient pressure tests, construct high pressure apparatus
  - Select Hlx distillation method for lab scale tests, construct Hlx section
  - Complete Bunsen reactor construction
- FY06 – Complete testing of three stand alone sections in preparation for integrated lab scale experiments
- FY07 – Assemble component sections, initiate closed loop testing
- FY08 – Perform S-I Hydrogen test program in integrated lab-scale apparatus

# Publications and Presentations

## Sulfur Iodine Thermochemical Cycle

### Presentations

- NHI Semiannual Reviews (September 2004, March 2005)
- UNLVRF High Temperature Heat Exchanger Program - Quarterly reviews

### Publications

- Bunsen Wong, et.al., "Construction Material Development in Sulfur-Iodine Thermochemical Water-Splitting Process for Hydrogen Production," AIChE Spring Meeting, April 2005, Atlanta
- Benjamin E. Russ, et.al., "HI Decomposition- A Comparison of Reactive and Extractive Distillation Techniques for the Sulfur-Iodine Process," AIChE Spring Meeting, April 2005, Atlanta
- Paul M. Mathias, Lloyd C. Brown, "Quantitative Analysis of the Sulfur-Iodine Cycle Through Process Simulation," AIChE Spring Meeting, April 2005, Atlanta
- Paul M. Mathias, Lloyd C. Brown, "Phase Equilibria and Thermodynamic Properties of the Sulfur-Iodine Cycle," AIChE Spring Meeting, April 2005, Atlanta
- Bunsen Wong, et.al., "Construction Material Development in Sulfur-Iodine Thermochemical Water-Splitting Process for Hydrogen Production," AIChE Spring Meeting, April 2005, Atlanta
- "Metallurgical and Corrosion Characterization of Structural Materials for the National Hydrogen Initiative", Ajit Roy, Radhakrishnan Santhanakrishnan, Ancila Kaiparambil, Bunsen Wong, Gottfried Besenbruch, Lloyd Brown  
Materials Science & Technology 2005, Symposium: Materials for the Hydrogen Economy, Sep. 25-28, 2005, Pittsburgh, PA
- Fred Gelbard and Paul Pickard, "Lab-Scale Catalytic Decomposition of Sulfuric Acid with Scalable Materials," AIChE Spring Meeting, April 2005, Atlanta
- Dion Rivera and M. Kathleen Alam, "In Situ Monitoring of Sulfuric Acid decomposition by Fourier Transform Infrared (FT-IR) Spectroscopy in the Sulfur Iodine Thermochemical Reaction for the Production of Hydrogen," Pittcon Analytical Conference, Feb. 28 - Mar. 4 2005, Orlando, Florida

### Other Reports

- Bunsen Wong, Lloyd C. Brown, Robert Buckingham, Gottfried Besenbruch, Gary Polansky, and Paul Pickard, "Engineering Materials Requirements Assessment for the SI Thermochemical Cycle," GA-A24902/SAND2004-681, February 2005.
- Lloyd Brown, Bob Buckingham, Ben Russ, Gottfried Besenbruch, Fred Gelbard, Paul Pickard, Jean-Marc Borgard, "Design of the Integrated Lab-Scale Experiment for the Sulfur-Iodine Thermochemical Cycle," INERI Report, September 30, 2004

# Hydrogen Safety

## **What is the most significant hydrogen hazard associated with this project?**

- The most significant hydrogen hazard is associated with a hydrogen explosion from the HI decomposition experiments.
- This could happen if hydrogen accumulates in large quantities in the equipment or the exhaust system and an ignition source is present.

# Hydrogen Safety

## What are you doing to deal with this hazard?

- Work is governed by General Atomics corporate safety program
- Requires development and approval of a Hazardous Work Authorization (HWA) before any experimental work can be initiated.
- Approval is given by independent Safety Committee, after detailed review of the HWA document.
- HWA details hazards and mitigation techniques. (Requirements include applicable Government and industry regulations).
  - Equipment designed to minimize the free hydrogen volume
  - Work performed in inerted environment.
  - Providing for air and Nitrogen dilution of hydrogen exhaust ports to keep the hydrogen concentration well below the explosive limit.
  - Equipment designed to eliminate potential ignition sources
  - Burst disc installed that vents into the chemical scrubber